

THE EFFECT ON DIESEL ENGINE EMISSIONS WITH HIGH CETANE ADDITIVES FROM BIOMASS OILS

D.W. Soveran, M. Sulatisky
Saskatchewan Research Council
515 Henderson Drive
Regina, Saskatchewan S4N 5X1
Canada

K. Ha, W. Robinson
ORTECH International
2395 Speakman Drive
Mississauga, Ontario
Canada

M. Stumborg
Agriculture Canada
P.O. Box 1030
Swift Current, Saskatchewan
Canada

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ABSTRACT: A process to convert plant oils (e.g. vegetable oils), tree oils (e.g. palm, tall oil) and other similar biomass oils to valuable high cetane blending components (supercetane) has been under development at the Saskatchewan Research Council (SRC) for approximately six years. The SRC recently completed a long-term conversion test (40 days) to demonstrate the process operability and catalyst activity maintenance. Sufficient product was generated for a fuel evaluation program that was performed at ORTECH International in Mississauga, Ontario. Two groups of blends were tested in a single cylinder diesel engine. The program compared the effects on fuel blends of converted vegetable oil and commercial cetane additives. The supercetane proved to be as effective as typical commercial additives. In addition, it was more effective on low cetane base fuels (e.g. light cycle oil) than commercial additives.

1. INTRODUCTION

The Saskatchewan Research Council has been performing research on the conversion of biomass oils into transportation fuels for more than a decade. In the mid-1980's the focus of the work turned to converting vegetable oils to diesel fuel. Convinced that the well-established conversion method of esterification of triglyceride oils was not attractive to conventional petroleum refiners, conversion techniques based on conventional petroleum conversion technology

were tested. The petroleum refining industry is a capital-intensive and complex. It was likely that an unconventional feedstock and an unknown conversion technology would have a difficult time finding acceptance within the industry. By developing a conversion method similar to those already in use at most refineries, renewable feedstocks would stand a better likelihood of utilization.

The first project demonstrated that hydroprocessing technology was flexible enough to convert triglyceride oils to a diesel fuel. Conversion products were expected to have cetane numbers in the 50-60 range (similar to esterified oils), but hydroprocessed vegetable oils have cetane numbers in the 90-100 range. It was quickly recognized that the product had more value as a diesel cetane improver. The process has since been patented.¹

Subsequent projects have continued the development of the conversion process. A variety of triglyceride oils (most plant and some tree oils) have been tested. Most limitations of the process have been determined. The actual chemistry of the conversion process is quite simple. Figure 1 provides a simple representation of the reactants and significant products. The fatty acid chains are broken off the triglyceride molecule, oxygen is removed (either as water or carbon dioxide), and any other double bonds saturated. A saturated paraffin is the predominant product. Other products include propane, carbon dioxide, carbon monoxide and water. As much as 85 wt. % of the feed is converted to a diesel product. The cetane value of the final product is a function of the fatty acid chain length. Most common vegetable oils have 16-20 carbon atom chains. This will yield a product with a cetane value of 90-100.

One non-triglyceride oil, tall oil, has been tested as well.² Derived from the pulping of pine trees, it is a mixture of free fatty acids and diterpene based compounds. The conversion product has a lower cetane value, around 70. Tall oil does have a very significant advantage though, it has a much lower cost than any vegetable oil.

In parallel to the experimental program, several economic analyses were performed to identify potential opportunities for application of this technology.^{2,3} The objective of this segment of the work was to find the applications available in the current energy market. Most renewable fuels (e.g. ethanol) rely on special tax breaks to be economically viable; getting these considerations for triglyceride oils would delay implementation of the technology. There was a belief at the SRC that there may exist economically attractive opportunities. A market survey of vegetable oil and other biomass oil production identified the plentiful and low cost oils. The most promising candidate, from a Canadian perspective, was tall oil. Canadian tall oil has a lower acid content than most other tall oils. Consequently, most is burned at the individual pulp mills because there is no market for the material.

Tall oil has become the focus of a commercial application in Canada. A process licence has been granted to a Canadian consulting company who is working with a tall oil fractionation company to develop a conversion facility.

Other economic analyses have identified potential scenarios for higher cost vegetable oils. These scenarios were directed to the situation faced by many Canadian refiners. With light oil production decreasing in Canada, refiners are having to use lower quality crude oils to meet their

market needs. The cetane value of many middle distillate products does not meet the requirements of the market. Cetane additives are relied on to bring these products to the necessary levels. Most commercial additives are expensive and cannot be added in the large quantities sometimes required. Some refiners are finding that it is necessary to hydrotreat their middle distillates to achieve the desired cetane numbers. One analysis has identified that it is much cheaper to hydroprocess a small volume of vegetable oil than it is to hydrotreat a large volume of middle distillate to reach the same cetane increase.

Because the conversion product is more than a straight diesel replacement, an accurate measure of its value is more difficult to determine. Some very limited engine tests indicated that conventional diesel fuels containing a small percentage of converted vegetable oil improved engine performance beyond those that could be attributed to the cetane number increase. For development to continue, a better definition of the product value was required.

This background information provides the basis for the work discussed in this paper. The areas to be covered include the demonstration of a longer operating period for the conversion process and a systematic program of comparing fuel blends.

2. EXPERIMENTAL

2.1 Production of Supercetane

Prior to this project the conversion process had been tested for short periods of time. Five days had been the longest period of operation. Catalyst deactivation was measurable in that short period. Although it was much quicker than conventional petroleum conversion, this problem was not expected to delay technology application. This project presented the opportunity to operate a conversion unit for a much longer period of time allowing some experimentation with techniques to prolong catalyst activity. To produce sufficient quantities for the engine testing, a larger laboratory hydroprocessing unit was operated for 45 days. Some techniques to alleviate catalyst deactivation were tested during this period.

Most of the developmental work was performed with a 30-mL trickle bed reactor system. A similar apparatus with a 100-mL trickle bed reactor was used for the project. Figure 2 provides a simplified schematic of the unit. The liquid product was collected at 24-hour intervals and analyzed for middle distillate content. Analysis of the gas product was done approximately three times per 24-hour period. Daily mass balances were performed to monitor conversion and product yields.

The feedstock for the conversion operation was canola oil. Canola oil (still called rapeseed oil in many other countries) is grown extensively in western Canada. It is a low euric acid oil, with a predominant fatty acid chain length of 18 carbon atoms. An analysis is provided in Table 1.

The liquid products were distilled at an outside laboratory to produce a middle distillate fraction boiling in the 210-343°C range. The distillation technique complied with ASTM method

D-2982. Approximately 120 L of conversion product (referred to as "supercetane" at SRC) was prepared. An analysis of supercetane is shown in Table 1.

2.2 Engine Testing

A systematic engine testing program was set-up with the advice of ORTECH International. When testing diesel fuels, several factors are investigated. Increasing environmental awareness is focusing most work on engine emissions. Unburned hydrocarbons, carbon monoxide, nitrous oxides and particulate emissions are the key items in fuel evaluation. Other factors tied to engine performance are included as well: fuel consumption, thermal efficiency and power output.

A single cylinder engine was utilized to perform steady-state emissions testing for six fuels containing various amounts of cetane improver. Engine test conditions selected corresponded with those required by EPA 13-mode testing. Gaseous and particulate emissions were collected during the 13-mode test conditions consisting of 5-modes at rated engine speed, 5-modes at an intermediate speed, and at idle speed of the engine. The EPA 13-mode test is a recommended practice for determining the gaseous emission levels of heavy-duty diesel engines and was adapted for the test program. Emissions collected were measured in accordance with the recommended Society of Automotive Engineers (SAE) practices.

Because of the small size of the test engine and its low exhaust flow rate, available dilution tunnel/particulate sampling equipment could not be used. For this reason, particulate sampling was conducted from the raw or undiluted exhaust of the engine. Figure 3 is a schematic of the system.

From the Ricardo engine manufacturer's performance curves, and from running the reference fuels, engine conditions were determined as shown in Table 2. The engine timing was set according to the engine manufacturer's specifications. The poor quality of the B reference fuel necessitated a timing change at idle conditions. The other blends in the B fuel group were also run at the same conditions as the B reference fuel. Engine timing was not optimized for the fuel blends tested.

The Saskatchewan Research Council supplied ORTECH International with a total of 210 L of each of the six fuels to be evaluated for engine emissions. The fuels were divided into two series, the first fuel of each series was identified as Reference A and Reference B. These were considered to be the baseline fuel for each series from which all emission comparisons were performed and calculated. The remaining fuels were identified as A1, A2, B1 and B2, respectively. Compositions of all the test fuels were made available to ORTECH after all testing was completed and results tabulated. This was to ensure that all testing performed was unbiased.

Two reference fuels were chosen with the aid of a Canadian refiner. The first was a typical commercial grade diesel with a cetane number of 43.6. The second was a low cetane, high aromatic content middle distillate (light cycle oil) obtained from the fluid catalytic cracking of gas oil (343-525°C). The light cycle oil (LCO) had a cetane value 31.7. Neither fuel had any

commercial cetane additives. From each reference fuel two blends were made. The cetane value was increased by four to 48 in the fuel A series. The LCO blends had the cetane number increased to 43 with the additives. Table 1 gives an analysis of each fuel blend, as well as the amount and type of cetane additive. A commonly used commercial cetane additive was used for comparison. It is based on an alkyl nitrate compound. The cetane value of the supercetane is 90.7. All cetane determinations were performed using the ASTM standard engine technique.

3. RESULTS AND DISCUSSION

3.1 Supercetane Production

The production of supercetane required 45 days of continuous operation. As many as three catalyst replacements were expected because of activity loss, but conditions were altered to maintain activity. Product yields and quality were kept at a constant level for almost the entire period of operation. A change in conditions was made at day 40. Changes in gas yields were observed by the end of the run indicating that activity was deteriorating.

Figure 4 summarizes the distillate, water and gas yield on a daily basis. Gas yields for the first three days of operation were quite low because of an undetected gas leak. Distillate yields were nearly stoichiometric for the entire run.

3.2 Engine Testing of the Fuel Blends

Evaluation of the different fuel blends was performed at ORTECH International in Mississauga. ORTECH is an internationally recognized engine and fuel testing facility. Most engine testing is now done on heavy-duty, multicylinder diesel engines. Producing sufficient supercetane for multi-cylinder engine analysis would have been too costly for the purposes of this project. The single cylinder Ricardo engine is a proven research tool which will provide reliable results. The data generated using this engine are not directly translatable to larger, more modern engines. It is, however, a useful tool for comparing the effects of different fuels on engine operation. The same trends would be observable on large multicylinder engines.

All the data reported were calculated using the EPA 13-mode weightings and calculations. Not all the information generated by the test program is presented here, only the more significant items of greatest interest (primarily emissions). Factors that also best illustrate the effect of the supercetane additive are also given.

Gas emissions are summarized in Table 3. Carbon dioxide (CO₂) emissions were similar for all the fuels with a cetane number above 40. The reference B fuel had a much higher CO₂ emission rate (per power output) than the other fuels. Fuels A1 and A2, those with the highest cetane number, had the lowest CO₂ emissions. A similar observation was possible with carbon monoxide (CO) emissions. The A1 and A2 blends were marginally better than A, B1 and B2 fuels. Total oxides of nitrogen were similar for all fuel blends.

Brake specific fuel consumption (BSFC) values were similar to the gaseous emission data. With the exception of the B reference fuel, which was higher, all the other fuels were very similar.

Total hydrocarbon emissions clearly showed the effect of increasing cetane values. The A1 and A2 blends had 10% lower emission rates. The B1 and B2 blends were similar to the A series fuels. Their emissions were 40% of the B reference fuel.

Particulate emissions are summarized in Table 4. Particulates are categorized as containing two separate fractions, a soluble (in methylene chloride) fraction and an insoluble fraction. The soluble fraction is considered to be more toxic because it will contain aromatic organic compounds, and therefore carcinogenic. For the A series fuels, the total particulates increased for the higher cetane blends. Almost all of the increase was in the insoluble fraction. The total particulates for the B blends decreased with the B1 and B2 fuels. The soluble fraction was reduced significantly while the insoluble increased by more than 100%.

The engine testing program provided reliable data on the effects of adding supercetane to conventional diesel fuel blends. Although its primary effect on fuel performance was related to the impact it had on cetane value, the project provided additional insights into what fuel characteristics have the most impact on engine emissions.

4. CONCLUSIONS

Improvements to the conversion process were developed in the project. A catalyst activity maintenance technique successfully kept the activity constant for 40 days of continuous operation. It is expected that catalyst life for this process will be similar to that used for hydrotreating of petroleum fractions (at least one year).

The fuel evaluation program proved that supercetane is an effective cetane improver for a wide range of middle distillate fractions. It can be blended to high or low cetane base fuels and have the same impact on cetane value. Commercial additives are less effective as the cetane number of the base fuels decreases.

Engine emissions are most affected by the cetane value of the fuel. Other researchers have also observed this phenomenon.^{4,5,6} In recent times there has been much concern focused on the aromatic content of diesel fuels and their contribution to emissions. The results clearly demonstrate that fuels produce similar emissions even though there are large differences in aromatic content. For example, the B2 fuel contains 38 vol % aromatics and A2 contains only 21.6 vol %, while emissions are very similar in almost every respect for these two fuels.

Supercetane does have two negative effects on the fuels it is added to. Both are related to the basic chemical nature of supercetane. Supercetane is a normal paraffin, boiling at the upper end of the middle distillate range, with 16-20 carbon atoms. Pure supercetane has a pour point of 21°C, which results in an increased pour and cloud point for each fuel it is added to. This limits its use in Canada and the northern United States to summertime fuel blends. It also limits the amount that can be blended with a fuel. Adding 8 vol % is all that is possible without

a dramatic effect on pour point. In the southern half of the United States it is less of a consideration.

Supercetane's high molecular weight also increases engine particulate emissions. Fortunately it increases only the insoluble portion, but since particulates are also quite visible it may make them appear less attractive.

The fuel evaluation study provided no evidence that the supercetane additive had other positive effects on engine performance other than those related to the cetane value increase. Limited engine testing done in other projects showed some performance benefits. These benefits were related to the higher cetane value of the fuel with supercetane added.

Development of this process is continuing at the Saskatchewan Research Council. A larger-scale pilot plant operation is in the planning stages. Further engine testing in large-scale multicylinder engines is expected to follow the pilot plant program. Other biomass oils such as waste animal oils and pyrolysis oils are being considered for evaluation. The commercialization with a tall oil feedstock is proceeding in parallel to these other activities. The SRC is also studying other potential applications.

ACKNOWLEDGEMENT

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REFERENCES

1. Craig, W.K., Soveran, D.W. **Production of Hydrocarbons with a Relatively High Cetane Rating**, United States Patent No. 4,992,605
2. Soveran, D.W., Coxworth, E., Craig, W.K., Uloth, V.C., McBride, G.E. **Conversion of Tall Oil Derivatives to Premium Quality Transportation Fuels**, Confidential Report to Energy, Mines and Resources Canada, 580 Booth Street, Ottawa, Ontario K1A 0E4, Canada
3. Soveran, D.W., Coxworth, E., Sulatisky, M., Robinson, W., Ha, K. **Fuel Properties and Engine Performance of Fuel Additives Produced by Hydrotreating Triglyceride Oils**, Confidential Report to Energy, Mines and Resources Canada, 580 Booth Street, Ottawa, Ontario K1A 0E4, Canada
4. Ullman, T.L., Mason, R.L., Montalvo, D.A. **Effects of Fuel Aromatics, Cetane Number, and Cetane Improver on Emissions from a 1991 Prototype Heavy-Duty Diesel Engine**, International Fuels and Lubricants Meeting and Exposition, Tulsa, Oklahoma, October 22-25, 1990

5. Sienicki, E.J., Jass, R.E., Slodowske, W.J. **Diesel Fuel Aromatic and Cetane Number Effects on Combustion and Emissions from a Prototype 1991 Diesel Engine**, International Fuels and Lubricants Meeting and Exposition, Tulsa, Oklahoma, October 22-25, 1990
6. Cunningham, L.J., Henly, T.J., Kulinowski, A.M. **The Effects of Diesel Ignition Improvers in Low-Sulfur Fuels on Heavy-Duty Diesel Emissions**, International Fuels and Lubricants Meeting and Exposition, Tulsa, Oklahoma, October 22-25, 1990

Table 1 Analysis of Canola Oil, Supercetane and Fuel Blends

Analysis	Canola	Supercetane	Fuel A	Fuel A1	Fuel A2	Fuel B	Fuel B1	Fuel B2
Density @ 15°C	920.4		824.0	820.6	824.0	860.9	844.3	859.8
Cloud Point (°C)		24	-29	6	-32	-38	8	-16
Pour Point (°C)		21	-47	-16	-47	-53	-4	-49
Sulphur (wt. %)	0.02	0.0015	0.032	0.026	0.027	0.023	0.018	0.025
Flash Point (°C)		138	63	62	63	75	76	75
Corrosion (Cu, 3 hr. @ 50°C)		none	none	none	none	none	none	none
Viscosity @ 40°C, cSt	37.0	3.74	1.74	1.91	1.76	1.92	2.25	1.97
Carbon Residue (wt. %)		0.05	0.08			0.24		
Ash (wt. %)		$< 2 \times 10^{-3}$	$< 2 \times 10^{-3}$			$< 2 \times 10^{-3}$		
Cetane number		90.7	43.6	47.7	47.7	31.7	43.3	42.3
Paraffins			15.8	23.5	16.0	4.7	23.7	13.2
Naphthenes			60.7	54.7	61.7	49.5	39.7	46.3
Olefins			1.0	0.7	0.7	1.3	1.3	2.4
Aromatics			22.5	21.1	21.6	44.5	35.3	38.1
Supercetane (vol %)				8.0			22.0	8.0
Cetane Additive (vol %)					0.1			0.2

Table 2 Engine Test Matrix

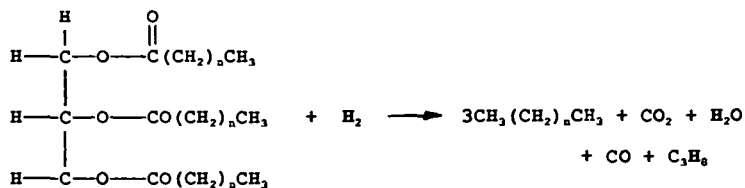
Fuel I.D.	Engine Test Conditions									
	Rated			Intermediate			Idle			
	Speed (rpm)	Torque (Nm)	Timing (°)	Speed (rpm)	Torque (Nm)	Timing (°)	Speed (rpm)	Torque (Nm)	Timing (°)	
A	3600	17.5	19	2400	18.5	16	780	1.8	14	
A1	3600	17.5	19	2400	18.5	16	780	1.8	14	
A2	3600	17.5	19	2400	18.5	16	780	1.8	14	
B	3600	17.5	19	2400	18.5	16	780	3.5	18	
B1	3600	17.5	19	2400	18.5	16	780	3.5	18	
B2	3600	17.5	19	2400	18.5	16	780	3.5	18	

Table 3 EPA 13-Mode Brake Specific Emissions (Gaseous)

Fuel I.D.	Total Hydrocarbons as CH ₄ (g/kW-hr)	% Change	Carbon Monoxide (g/kW-hr)	% Change	Total Oxides of Nitrogen (g/kW-hr)	% Change	Carbon Dioxide (g/kW-hr)	% Change
A	6.74	-	8.90	-	9.53	-	1140	-
A1	6.09	-10	6.97	-22	8.32	-13	1145	0
A2	6.08	-10	6.47	-27	9.21	-3	1153	1
B	15.64	-	23.89	-	9.94	-	1316	-
B1	5.83	-63	7.33	-69	9.50	-4	1192	-9
B2	6.39	-59	7.23	-70	10.08	1	1176	-11

Table 4 EPA 13-Mode Brake Specific Emissions (Particulates)

Fuel I.D.	Total Parts (g/kW-hr)	% Change from Base Fuel	Soluble Fraction (g/kW-hr)	% of Total Part.	% Change from Base Fuel	Insoluble Fraction (g/kW-hr)	% of Total Part.	% Change from Base Fuel
A	0.472	-	0.188	40	-	0.284	60	-
A1	0.588	25	0.196	33	4	0.392	67	38
A2	0.574	22	0.192	33	2	0.382	67	35
B	1.358	-	1.035	76	-	0.323	24	-
B1	1.123	-17	0.301	27	-71	0.822	73	154
B2	0.919	-32	0.233	25	-77	0.686	75	112



Triglyceride Molecule, $n=14$ to 18

Figure 1 Conversion Reaction for Supercetane Production

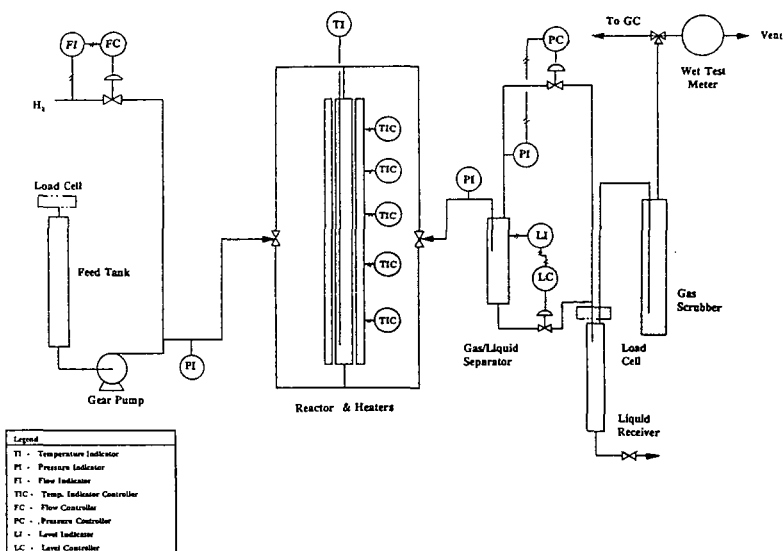


Figure 2 Schematic of Laboratory Hydroprocessing Unit - 100-mL Reactor.

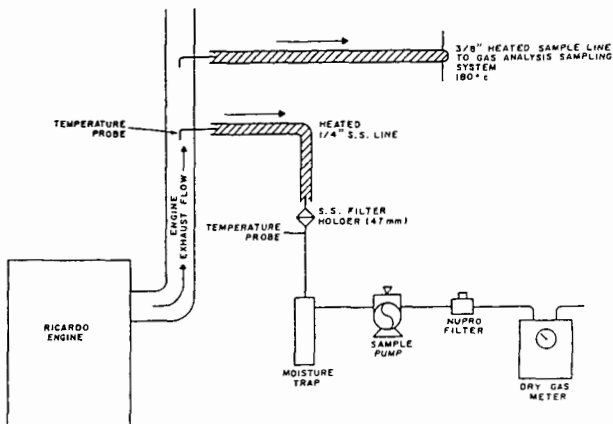


Figure 3 Particulate Sampling System - Ricardo Test Engine

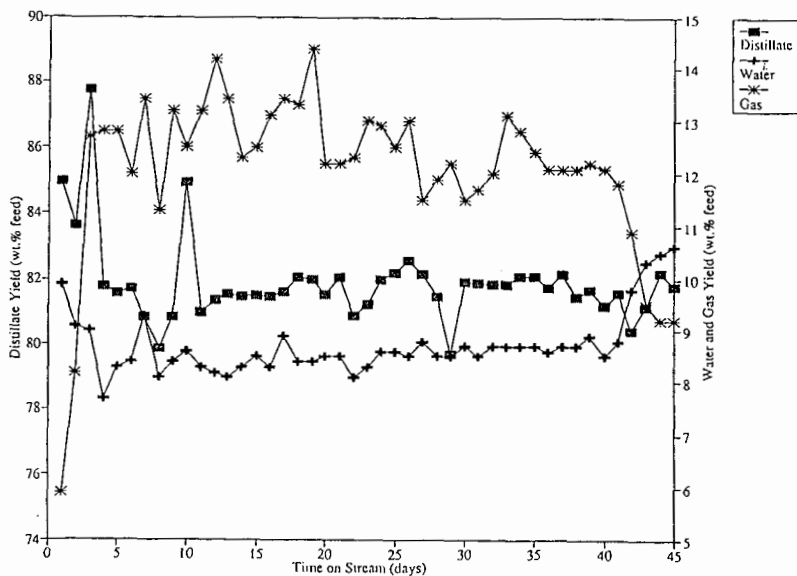


Figure 4 Liquid and Gas Yield Summary - Supercetane Production